

Electronic structure, disconnected Fermi surfaces and antiferromagnetism in the layered pnictide superconductor $\text{Na}_x\text{Ba}_{1-x}\text{Ti}_2\text{Sb}_2\text{O}$

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We report electronic structure calculations for $\text{BaTi}_2\text{Sb}_2\text{O}$ and discuss the results in relation to the observed superconductivity of this material when hole doped with Na. The Fermi surface shows several sheets. These include a nested nearly 2D cylinder. There are also two sheets, which are three dimensional, in spite of the layered crystal structure. A magnetic instability associated with Fermi surface nesting is found. A sign-changing s -wave state, different from the one in the Fe-based superconductors, is predicted within a scenario of spin-fluctuation mediated superconductivity.

The discovery of high temperature superconductivity in Fe-based compounds¹ has lead to renewed interest in non-oxide superconductors. Recently, Doan and co-workers² reported superconductivity in $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$, $0.05 \leq x \leq 0.33$ and T_c up to 5.5 K. The structure of the parent compound, $\text{BaTi}_2\text{Sb}_2\text{O}$, as determined by x-ray refinement,² is shown in Fig. 1. This structure shares a number of common features with the Fe-based superconductors. Specifically, it is a layered structure containing square planes of transition element atoms, in this case Ti. Like the Fe-based superconductors, there are two transition metal atoms per chemical unit cell. As may be seen, the two Ti in the $\text{BaTi}_2\text{Sb}_2\text{O}$ unit cell are related by a translation of $[1/2, 1/2]$ followed by a 90° rotation, and not by the glide of the Fe_2As_2 layers in the Fe-based superconductors. Superconductivity was also very recently reported by Yajima and co-workers in undoped $\text{BaTi}_2\text{Sb}_2\text{O}$ with a bulk T_c of 0.8 K.³

The nearest neighbor Ti-Ti distance is 2.91 Å, which is only somewhat larger than the nearest neighbor distance of 2.51 Å in Ti metal, implying the possibility of important direct Ti-Ti bonding, as for the Fe lattice in Fe-based superconductors.⁴ Also similar to the Fe-based superconductors each Ti atom is coordinated by four pnictogens, although in the present case the geometry is that of approximate square planes with Ti at the center, instead of approximate tetrahedra and furthermore, no Fe-based superconductor is known where the pnictogen is Sb. Furthermore, the Ti are also coordinated by O in the present compound. Each Ti has two O nearest neighbors. Thus as shown in the right panel of Fig. 1, if one considers only Ti-O hopping, one obtains a bipartite lattice consisting of two independent sets of one dimensional $\dots\text{Ti-O-Ti-O}\dots$ chains, running respectively along x and y . Similarly if one considers only Ti-Sb hopping one also obtains one dimensional chains, $\dots\text{Ti-Sb}_2\text{-Ti-Sb}_2\dots$, running along y and x where Sb_2 denotes an Sb above the plane and an Sb below the plane. Such 1D objects might therefore form the basis of a strongly nested electronic structure. However, as mentioned, the short Ti-Ti nearest neighbor distance suggests metal-metal bonding, which would couple the two sub-lattices. Furthermore the Sb atoms are arranged in linear chains along the c -axis with Sb-Sb distances of $\sim c/2 = 4.05$ Å, which is short enough that c -

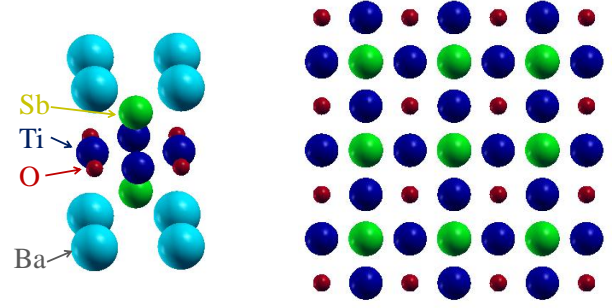


FIG. 1. Layered structure of $\text{BaTi}_2\text{Sb}_2\text{O}$ (left) and as viewed along the c -axis with the Ba spheres suppressed (right).

axis hopping could be important, especially assisted by the Ba. Returning to the metal-metal bonding, one sees that the bonds run along the diagonal directions in the two Ti atom unit cells, i.e. forming a square network oriented at 45° to the $\dots\text{Ti-O-Ti-O}\dots$ and $\dots\text{Ti-Sb}_2\text{-Ti-Sb}_2\dots$ chains.

Experiments² show that stoichiometric $\text{BaTi}_2\text{Nb}_2\text{O}$ has a transition at $T_s = 54$ K, similar to several other related compounds.⁵⁻⁹ This transition has strong signatures in resistivity, susceptibility and specific heat. The microscopic mechanism for this transition has not been demonstrated, but it is described as either a charge density wave (CDW) or a spin density wave (SDW). This is consistent with electronic structure calculations for the compound $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$, which show a nested Fermi surface.¹⁰

In any case, as Na is substituted for Ba in $\text{Na}_x\text{Ba}_{1-x}\text{Ti}_2\text{Sb}_2\text{O}$, T_s is systematically suppressed and superconductivity arises with T_c of up to 5.5 K.² Importantly, superconductivity co-exists with the phase corresponding to T_s including near the maximum T_c . Superconductivity occurs for $0.05 \leq x \leq 0.33$, which nominally amounts to average Ti valences between $\text{Ti}^{3.025+}$ and $\text{Ti}^{3.165+}$ assuming that Sb occurs as Sb^{3-} . Titanates with valences between $4+$ and $3+$ are known to have electron-phonon superconductivity as in the case of electron doped SrTiO_3 ,¹¹ but they can also be magnetic and

exhibit non-trivial correlation effects as in e.g. TiOCl and LaTiO₃.^{12,13}

Here we report first principles studies of BaTi₂Sb₂O in relation to magnetism and superconductivity. We find that like its sister compound Na₂Ti₂Sb₂O, the Fermi surface is nested. This nesting leads to peaks in the susceptibility that are incommensurate but near the *X* points. These peaks are strong enough to result in an actual magnetic instability, which we confirm by direct calculations. This shows that T_s is most likely an SDW instability. Therefore the superconductivity of doped BaTi₂Sb₂O is in proximity to an antiferromagnetic SDW phase. This leads to a specific prediction of the pairing state in a spin-fluctuation mediated scenario, in particular a sign changing *s*-wave state, but not the same one as in the Fe-based superconductors.¹⁴

The electronic structure was calculated using standard density functional theory based on the Perdew, Burke, Ernzerhof generalized gradient approximation.¹⁵ For this purpose we used the general potential linearized augmented plane wave method including local orbitals¹⁶ as implemented in the WIEN2k code.¹⁷ The LAPW sphere radii were 2.4 bohr for Ba and Sb, 2.15 bohr for Ti and 1.7 bohr for O. The calculations are based on the experimental crystal structure.² This structure contains one internal coordinate, $z_{\text{Sb}}=0.2514$ corresponding to the Sb height. The value obtained from total energy minimization of $z_{\text{Sb}}=0.2522$ is very close to the experimental value. This is in contrast to the large discrepancies found in the Fe-based superconductors in standard non-magnetic density functional calculations.¹⁸ We used well converged LAPW basis sets, including additional local orbitals, along with dense Brillouin zone samplings, as high as a 48x48x24 mesh for the primitive tetragonal cell.

The calculated band structure is shown in Fig. 2 and the corresponding electronic density of states (DOS) is shown in Fig. 3 along with projections. These calculations were done relativistically, including spin-orbit, but spin-orbit does not have a large effect. It does, however, affect the details at E_F . A comparison of the DOS with and without spin-orbit is given in Fig. 4.

The value of the DOS at the Fermi energy (with spin-orbit) is $N(E_F)=4.26 \text{ eV}^{-1}$ on a per formula unit basis. This corresponds to a bare specific heat $\gamma=10.0 \text{ mJ mol}^{-1}\text{K}^{-2}$ and bare Pauli susceptibility $\chi_0(\mathbf{q}=0)=1.37\times 10^{-4} \text{ emu/mol}$. The calculated Drude plasma energies are $\hbar\Omega_{p,xx}=2.71 \text{ eV}$ and $\hbar\Omega_{p,zz}=2.14 \text{ eV}$ for the in-plane and *c*-axis directions, respectively. For isotropic scattering this implies a resistivity anisotropy of ~ 1.6 , meaning that from a transport point of view this is a very 3D material. This is reminiscent of what was found previously by Pickett for the related compound Na₂Sb₂Ti₂O.¹⁰

The density of states shows that the O 2*p* derived bands lie between $\sim -7 \text{ eV}$ and -5 eV , while the Sb 5*p* bands are in the energy range $-4 \text{ eV} - -1 \text{ eV}$, all with respect to E_F . Therefore, these shells are nominally full. Also there are no Ba derived occupied valence bands.

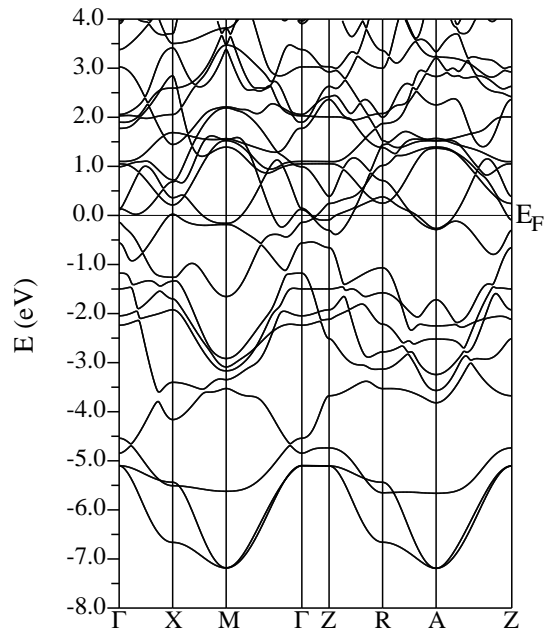


FIG. 2. Calculated band structure of BaTi₂Sb₂O including spin orbit. The Fermi energy is denoted by the horizontal line at 0 eV.

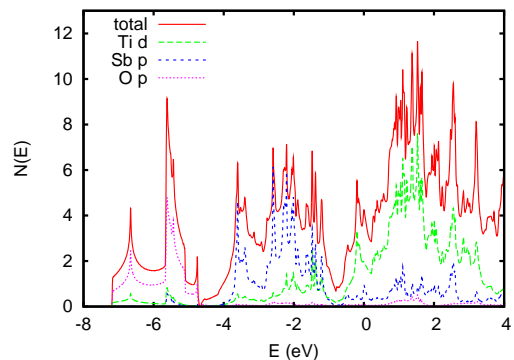


FIG. 3. Electronic density of states and projections onto the LAPW spheres.

Thus Sb is a trivalent anion in this compound and Ti is in its trivalent d^1 state. The density of states around E_F is derived primarily from Ti *d* states, hybridized with Sb *p*.

The orbital character is illustrated in Fig. 5, which shows the band structure in a 1 eV range around E_F emphasizing the character of different *d*-orbitals in a so-called “fat bands” scheme, where the bands are shown with symbols having a size that is a small value to make all bands visible plus an enhancement of the size proportional to the projection of given orbital character onto the

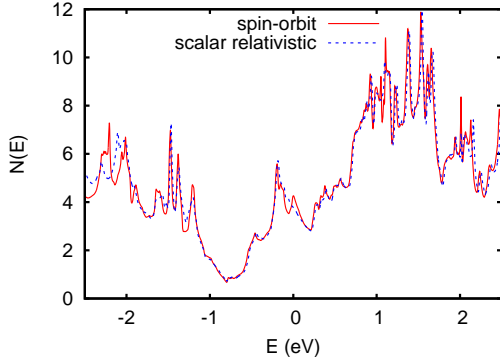


FIG. 4. Comparison of the density of states around E_F with and without spin orbit.

LAPW sphere. As may be seen, there are three d orbitals – d_{z^2} , $d_{x^2-y^2}$ and d_{xy} – that contribute significantly at E_F . There is strong d_{xy} character in this mixture.

The Fermi surface is shown in Fig. 6 and the dependence on band filling is given in Fig. 7. There are three sheets of Fermi surface. The first is a very two dimensional, square electron cylinder around the zone center. As seen in the fat bands plot, the band making up this cylinder contains a mixture of the three d orbitals that participate at E_F . There is a three dimensional complex shaped electron section around the $\Gamma - Z$ line. This section has d_{z^2} character. Finally, there is a large three dimensional hole section around X . Like the square cylinder electron section, this part of the Fermi surface has mixed character derived from the three active d -orbitals, though the dominant character is d_{z^2} . Since the electron count is even, this section compensates the two electron sections. This basic structure is preserved as the Fermi level is lowered within the range corresponding to superconductivity in $\text{Na}_x\text{Ba}_{1-x}\text{Ti}_2\text{Sb}_2\text{O}$. The hole section grows, while the two electron sections shrink. Importantly, the square cylindrical shape of the 2D section is preserved.

An important aspect of the Fermi surface is that the square section, as well as the edges of the X centered electron section are nested along the $[1,1]$ direction. The 2D nesting vector is approximately $(0.24, 0.24)(2\pi/a)$. $[1,1]$ is the orientation of the Ti square lattice. In this lattice, the d_{xy} orbitals are along the Ti-Ti bond directions, and may be expected to give nested bands. Actually, the nested electron section has strong d_{xy} , but also as mentioned involves the other two active d orbitals. In any case, qualitatively the nesting found should lead to two ridges in the bare susceptibility χ_0 running along the diagonals in the zone. The intersection near the X points would give a prominent peaks in $\chi_0(\mathbf{q})$ near the X points. This in fact is the case. Fig. 8 shows the bare Lindhard χ_0 calculated with the neglect of the ma-

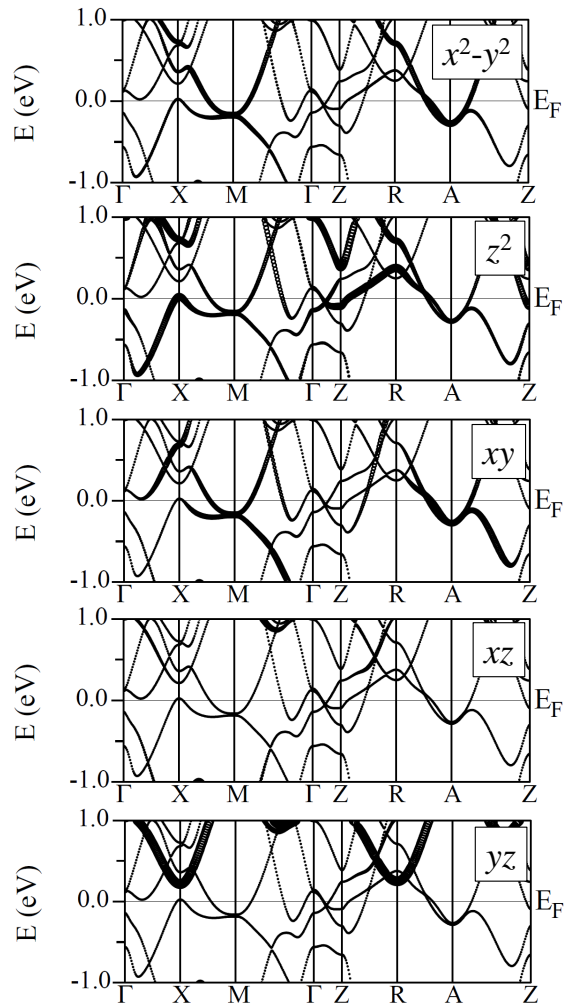


FIG. 5. Fat bands plot for different d orbital characters near E_F . The coordinate system is such that d_{z^2} is directed along the c -axis, and x and y are along the a -axis and b axis, such that d_{xz} is towards the nearest Sb and y is in the direction of the O neighbors.

trix element approximation, similar to calculations presented for the Fe-based superconductors.¹⁴ As seen there are diagonal ridges in the real part of χ_0 , with a prominent peak at X . This peak will be further increased by the RPA enhancement, $\chi(\mathbf{q}) = \chi_0(\mathbf{q}) / (1 - I(\mathbf{q})\chi_0(\mathbf{q}))$ (here $I(\mathbf{q})$ is written as a Stoner term, but in correlated materials it takes the form of the Hubbard parameter U).

The real part of χ governs magnetic ordering as well as providing the pairing interaction in spin-fluctuation induced superconductivity.^{19,20} We discuss it further below. The imaginary part of χ_0 , like the real part, shows ridges with intersections near X , but the structure is more complex. This structure in both the real and imaginary parts of χ , *i.e.* intersecting ridges with peaks at the intersections, is a consequence of the Fermi surface structure, particularly the square cylinder shape. This Fermi

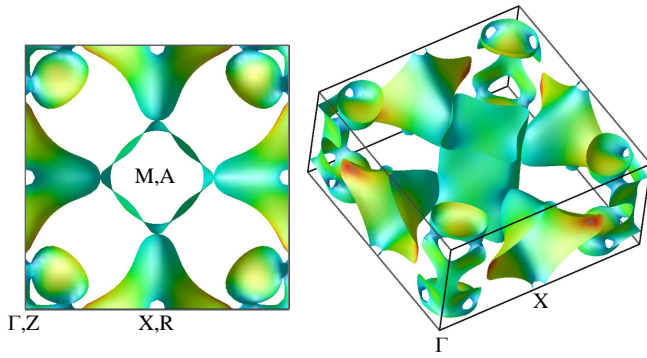


FIG. 6. Calculated Fermi surfaces of BaTi₂Sb₂O spin orbit. The shading is by velocity, with blue representing low velocity. The approximately square cylindrical sections around the zone corner (M,A) are electron sections as is the complex shaped section around Γ and Z. The other section around R is a hole section.

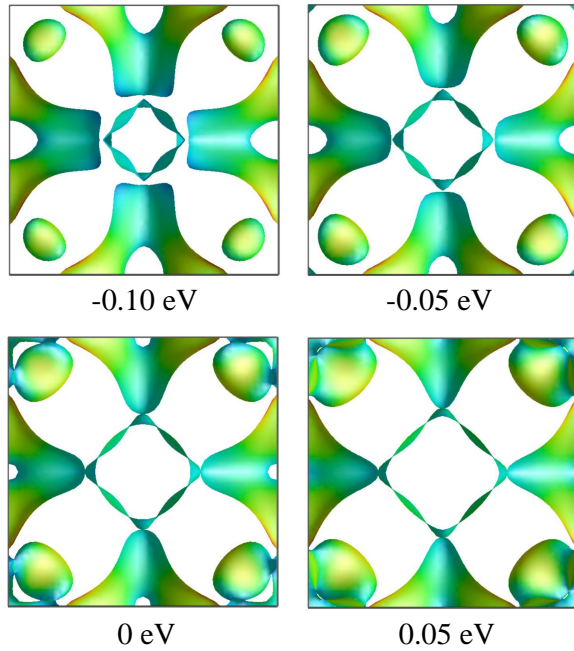


FIG. 7. c -axis view of the Fermi surface as in Fig. 6, but with shifted Fermi energies. The corresponding band fillings are -0.38 e (-0.10 eV), -0.23 e (-0.05 eV), 0 e (0 eV), and 0.20 e (0.05 eV).

surface amounts to the intersection of two 1D sections. The result is similar to the antiferromagnetic peak in the triplet superconductor Sr₂RuO₄,^{21,22} but different from the Fe-based superconductors where the nesting arises from matching of electron and hole Fermi surface sections.

We did direct self-consistent calculations to look for a magnetic ground state. We find a magnetic instability at the X point. These calculations were done including spin-orbit with the moment directed along the c -axis.

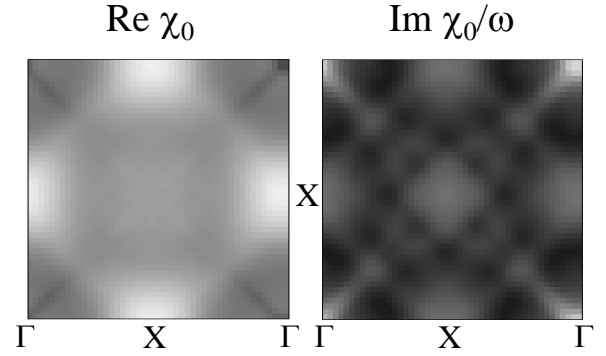


FIG. 8. Calculated c -axis projections of the real and imaginary parts of χ_0 (see text) with arbitrary units. Light shading denotes higher values.

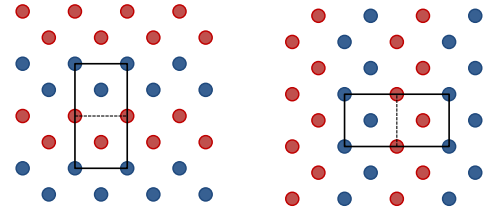


FIG. 9. Magnetic structure of the X -point ordering showing the two degenerate cases in the left and right panels. The doubling of the unit cell is shown. Red and blue denote up and down spins, respectively. Note the alternation of ferromagnetic and antiferromagnetic bonds in this double stripe structure.

We find an instability, with small Ti moments inside the LAPW spheres of $0.2 \mu_B$. This is much smaller than the $\sim 2 \mu_B$ characteristic of the Fe-based superconductors in similar calculations using the experimental crystal structure.¹⁸ We also checked for a nearest neighbor antiferromagnetic state, which would correspond to a zone center instability. However, we did not find such a state.

The magnetic structure is shown in Fig. 9. This is a so-called double stripe structure. It lowers the symmetry from tetragonal to orthorhombic and contains both ferromagnetic and antiferromagnetic Ti-Ti bonds, as shown. This may be expected to result in a spin-dimerization, with coupling to the lattice, perhaps consistent with neutron scattering results showing lattice anomalies at T_s in Na₂Ti₂Sb₂O.⁸ The actual magnetic structure may be incommensurate, as the moments are small and as mentioned, the intersection of the ridges in $\chi(\mathbf{q})$ is off the X point. Another indication that the actual ground state may be a more complex incommensurate magnetic structure is that in our calculations without imposed symmetry for the X point instability we find slightly different moments on the two Ti sites of each spin (the magnetic unit cell contains four Ti atoms, two spin-up and two spin-down).

In any case, we find a significant coupling of the magnetic order to the electrons at the Fermi energy. In particular, even though the moments are small, the DOS near E_F is substantially reduced in the ordered state. We find $N(E_F)=3.42 \text{ eV}^{-1}$ per formula unit for the X point ordered state as compared to $N(E_F)=4.26 \text{ eV}^{-1}$ without magnetic order. As in the Fe-based superconductors,²³ and in contrast to cuprates, the antiferromagnetic state near superconductivity is metallic, both in experiment² and in the present density functional calculations.

One of the reasons why unconventional superconductivity attracts so much attention is that it is a rare phenomenon. In particular, the vast majority of known superconductors are conventional electron-phonon superconductors, and in particular conventional electron-phonon superconductivity is known in titanates. Unlike the Fe-based superconductors, the maximum $T_c=5.5 \text{ K}$ observed in $\text{BaTi}_2\text{Sb}_2\text{O}$ is not so high as to preclude conventional superconductivity. However, the close proximity to an antiferromagnetic state provides an indication that this may not be the case. In particular, spin-fluctuations provide a repulsive interaction in a singlet channel, opposite to the attractive electron-phonon interaction. Therefore the net superconducting interaction will be $\lambda = \lambda_{ep} - \lambda_{sf}$, where ep and sf denote electron-phonon and spin-fluctuation contributions, respectively. As such the wide coexistence, of magnetic and superconducting order in the composition dependent phase diagram argues against (but does not fully exclude) conventional superconductivity. An argument against an unconventional state would be that scattering due to disorder in the alloy should suppress an unconventional state. However, the disorder in the present case is in the Ba layer, and as mentioned Ba does not contribute significantly to the electronic structure near E_F , and furthermore, as mentioned the bands are rather flat, which means that the superconducting coherence length will be relatively short, again reducing the effect of disorder.

As such, we discuss the possibility of a spin-fluctuation mediated unconventional superconducting state. In such a scenario, the pairing interaction is related to the real part of the actual RPA enhanced $\chi(\mathbf{q})$ and is repulsive for a singlet state and attractive for a triplet state.^{19,20,24} As mentioned, in $\text{BaTi}_2\text{Sb}_2\text{O}$ the susceptibility is peaked near X . Identification of the superconducting state amounts to matching the pairing interaction with the Fermi surface structure, so that opposite sign order parameters occur on parts connected by peaks in the repulsive (singlet case) interaction or parts connected by peaks in the attractive (triplet case) interaction have the same sign order parameter, while maintaining consistency with the overall triplet or singlet parity. We find that the best match is obtained for a singlet state as depicted in Fig. 10. In this state the two sections of Fermi surface with similar orbital character, namely the square section and the large section around X , have opposite sign as expected in such a scenario.

As seen, this is a sign-changing s -wave state, although

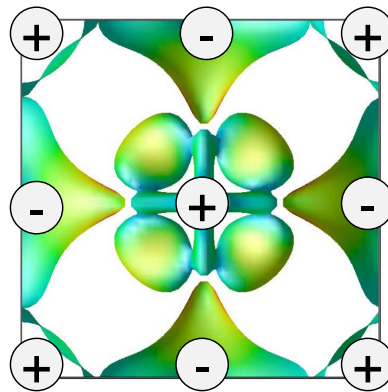


FIG. 10. Potential sign changing s -wave superconducting state, shown on top of the Fermi surface. Note that in this figure, Γ is at the center, as opposed to the corners of the plot.

not the same one as in the Fe-based superconductors. It consists of a state where the two electron sections of the Fermi surface have opposite sign order parameter to the large hole section. The motivation for this state is that it has sign changes between all pairs of Fermi surface sections that are separated by $(0, \pi/a)$ and $(\pi/a, 0)$, where the susceptibility is peaked. Similar to the Fe-based superconductors, the SDW and this superconducting state are competing instabilities of the Fermi surface. However, the SDW antiferromagnetism found for $\text{BaTi}_2\text{Sb}_2\text{O}$ is much weaker than that in the Fe-based superconductors. It is unclear what role correlation effects beyond standard density functional calculations play in these titanates. The fact that the transition at T_s is a metal-metal transition in spite of the integral band filling suggests that they are not so strong as in *e.g.* the cuprates. This of course is an expected result considering that the d orbitals in Ti^{3+} ions are more extended than those in Cu^{2+} . One possible effect of Coulomb correlations will be to enhance the small moments found here. It will be of interest to perform neutron diffraction experiments both to confirm whether the transition is in fact an SDW and to quantify the magnitude of the moments. In this regard, Subedi has recently presented electron-phonon calculations²⁵ that are consistent with electron-phonon superconductivity and so either scenario is possible here.

Returning to $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$, that material,²⁶ which has been studied more extensively than $\text{BaTi}_2\text{Sb}_2\text{O}$, has not been reported to show superconductivity, but does have a transition, likely of spin density wave or charge density wave character and a similar phenomenology to $\text{BaTi}_2\text{Sb}_2\text{O}$. The transition in $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ is at higher temperature, $T_s \sim 114 \text{ K} - 120 \text{ K}$.⁵⁻⁸ From a structural point of view, $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ has similar $\text{Ti}_2\text{Sb}_2\text{O}$ layers to $\text{BaTi}_2\text{Sb}_2\text{O}$, but these are stacked differently along the c -axis so that the Sb-Sb linear chains in the Ba compound are broken up yielding a body centered tetragonal structure. The band structure, which as mentioned has similarities to the present compound, was investigated

by Pickett using density functional theory, and in a tight binding framework by de Biani and co-workers.²⁷ The arsenide, $\text{Na}_2\text{Ti}_2\text{As}_2\text{O}$ has a transition at $T_s \sim 320$ K.⁶ Other related compounds may be $(\text{SrF})_2\text{Ti}_2\text{Sb}_2\text{O}$, which has an apparently similar phase transition at $T_s \sim 198$ K and $(\text{SmO})_2\text{Ti}_2\text{Sb}_2\text{O}$ with $T_s \sim 230$ K.²⁸ $\text{BaTi}_2\text{As}_2\text{O}$ also has been reported and has similar transition at $T_s \sim 200$ K. Considering the superconductivity of $\text{BaTi}_2\text{Sb}_2\text{O}$, it will be of great interest to study these compounds in more detail and especially their properties if the SDW can be suppressed, e.g. by pressure, doping or chemical substitutions. It will be particularly interesting to study the pressure dependence in $\text{BaTi}_2\text{Sb}_2\text{O}$ and related materials.

In conclusion, we find that $\text{BaTi}_2\text{Sb}_2\text{O}$ has an SDW instability associated with Fermi surface nesting. The close proximity of the superconducting phase that emerges

with Na doping to this antiferromagnetic phase suggests the possibility of unconventional spin-fluctuation mediated superconductivity. We find that the susceptibility is peaked near the X point. Matching this structure of the susceptibility with the Fermi surface suggests the possibility of a sign-changing s -wave superconducting state of a different nature than the Fe-based superconductors.

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